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EFFECT OF PLASTICIZERS ON THE STRENGTH OF A PLASTIC MOTOR CASE

PART II
EXTENSION AT BREAK OF RINGS TREATED WITH PLASTICIZER

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U.S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama

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Propulsion Systems Engineering Branch
Army Propulsion Laboratory and Center
Research and Engineering Directorate (Provisional)
U. S. Army Missile Command
Redstone Arsenal, Alabama 35809

ABSTRACT

This report contains the results of an investigation on the effects of seven plasticizers on the elongation at break point of rings cut from a glass-fiber-reinforced plastic motor case.

The rings were stored for over a year with a saturated mixture of fuller's earth and triethylene glycol dinitrate, tributyl phosphate, triethyl phosphate, dipropyl adipate, dibutyl phthalate, dibutyl maleate, or ethyl nonanoate. A blank was also used.

The extension at break was greatest for the blank and for triethylene glycol dinitrate. With other plasticizers there was significantly less extension at break.

The investigation is continuing using unlined motor cases packed with a mixture of sand and selected plasticizer. The actual burst strength will be investigated.

CONTENTS

ILLUSTRATIONS

SYMBOLS

$\overline{M}$	molecular weight
σ	surface tension (dynes/cm)
D	dipole moment
μ	viscosity (g/cm^3-sec)
ρ	density (g/cm)
∂	solubility factor $\left(cal^{1/2}/cm^{3/2}\right)$
G	hydrogen bonding factor, wavelength shift

1. Introduction

This work is a continuation of that described in U. S. Army Missile Command Report No. RK-TR-6,-1 as Phase I [1]. In this prior report seventeen commercial plasticizers used in the manufacture of solid propellants were rated by their effect on the shear creep of segments of rings cut from glass-wound epoxy resin motor cases. The effects of air and water were also determined in the same experiment.

The motor cases had 3 inches inside diameter and 10 inches overall length. The case consisted of 734 ends of S-glass per circumferential inch in helical winding only. Helix angle was 45 degrees. Sizing used was a silane, S-901. These motors had an average burst strength of 2605 psi. Ninety-five percent of the cases burst ±6 percent of the average at a confidence level of 90 percent. Further information about these cases can be found in the pertinent manufacturer's report [2].

The results of Phase I showed that the cumulative sag of the coupon was directly proportional to the surface tension of the plasticizer and inversely proportional to the viscosity. Properties such as dipole moment, hydrogen bonding, and solubility factor were not significant. This indicates that the penetration was a purely physical process. This type of penetration is explained more fully by Crank and Park [3]. A seemingly anomalous decrease in accumulative sag in the case of certain butyl esters at the higher temperature corroborated findings of A. K. Doolittle [4].

2. Research Plan and Materials

The effect on rings cut from the motor cases of those plasticizers found active in the first phase is investigated in this second phase. These rings were 3 inches inside diameter by 0.500 ±0.005 inches wide by 0.055 ±0.005 inches thick and were cut dry from the cylindrical portion of motor cases from the same lot as in Phase I. All raw edges were sealed with epoxy resin.

Seven plasticizers were selected from Phase I to be used in Phase II. Basis of selection was the greatest amount of deformation of the segment. The plasticizers selected were triethyl phosphate, tributyl phosphate, ethylnonanoate, dipropyl adipate, dibutyl phthalate, dibutyl maleate, and triethylene glycol dinitrate. These plasticizers were also from the same lots as used in Phase I.

Simulated propellants were prepared by absorbing these plasticizers on fuller's earth in the proportion of one mol of plasticizer to 533 grams of fuller's earth. All simulated propellants were definitely moist with plasticizer except

that containing triethyl phosphate which was damp only. The schedule called for tests at the two temperatures of storage, 76° and 140°F; at six time intervals at 76°F and three time intervals at 140°F; and for all tests to be run in triplicate. Blank tests were also to be run. The storage area for the 76°F test was a constant temperature, 50 percent relative humidity room. Storage area for the 140°F test was a test cabinet kept at that temperature.

Rings were packed with simulated propellant and stored between glass plates. Nine rings containing one composition were stored together. Plates were stored one tier high at 140°F and no more than two tiers high at 76°F. Rings stored at 76°F were packed with fuller's earth mixtures containing triethyl phosphate, tributyl phosphate, dibutyl phthalate, ethyl nonanoate, dipropyl adipate, or triethylene glycol dinitrate. Rings stored at 140°F contained mixtures with triethyl phosphate, dibutyl pthalate, dibutyl maleate, ethyl nonanoate, or dipropyl adipate. Unpacked rings for blanks were stored concurrently at each temperature.

Table I [5-8] gives the physical properties of the plasticizers used in this phase of the experiment.

TABLE I. PHYSICAL PROPERTIES

Plasticizer	$\bar{M}$	σ*	D [5, 8]	μ*	δ [6, 8]	ρ*	G [7, 8]
Triethyl phosphate	182	32.4	3.00	1.8	9.2	1.068	11.7
Tributyl phosphate	266	30.0	3.07	3.71	8.5	0.971	11.7
Ethyl nonanoate	186	29.2	1.75**	2.5	7.3	0.860	8.4**
Dipropyl adipate	230	33.2	2.40**	4.[illegible]	7.3	0.979	8.4**
TEGDN	240	47.2	2.99**	5.95	10.1	1.317	2.2**
Dibutyl phthalate	278	36.2	2.75	11.3	9.3	1.042	6.3
Dibutyl maleate	228	32.9	2.56**	4.0	8.5	0.988	8.4**
Epoxy resin	-	-	2.23**	-	10.9 ±2.4**	--	24.0**

* Measured at 76°F

** Estimated

3. Test Equipment and Methods

The original scheme of testing contemplated using a hydraulic method adapted from that developed by Naval Ordnance Laboratory (NOL) [9].

A modified hydraulic tester was made. However, during preliminary testing it was found that the amount of stretch in the rings on pressurizing, because of lack of circumferential wraps, was so great that about half the time the seal between the elastic obturator ring and the test fixture was lost, ruining the test. Since the test was set up statistically with three replicates, this entailed too great a loss of confidence and the hydraulic method was abandoned.

A split-D tester of normal design was therefore made for use in a Houndsfield Tensometer* and proved acceptable. This tensile tester can give a permanent record of the relationship between stress and extension.

All tests were conducted at 76°F and 50 percent relative humidity. Test rings were brought into the area, wiped, and allowed to temper for at least 30 minutes. They were then placed on the split-D tester and loaded into the machine. Rate of crosshead advance was approximately 0.3 inch per minute. All rings were stressed to rupture. Rings were then examined and data from those rings obviously breaking in a resin-poor area were rejected. These amounted to some 5 percent of the total number of rings.

Figures 1 and 2 show typical graphs of stress elongation, selected from several actual runs. Figure 1 shows the typical variation in the stress-elongation curves for rings in contact with dipropyl adipate for various lengths of time. Figure 2 shows the variation in the stress-elongation curves for various plasticizers at 12 months. In each instance, the curves start with zero force and zero elongation.

4. Results

Several criteria were examined to determine if one could differentiate between plasticizers. Breaking strength of the rings, extension of the rings at break, and ratio between applied stress and extension were investigated statistically. Only extension at break was found to give satisfactory results. Breaking strength was also found to correlate directly with extension at break, but the statistical evaluation of breaking strength as a criterion of difference between plasticizers was at a lower confidence level.

Table II gives the breaking strength and extension at break of rings stored at 76°F for various plasticizers at increasing time intervals. Values of

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*The use of this trade name is for identification purposes only and is not to be construed as a recommendation of this particular instrument.

MATERIAL:
COMPOSITE
COMPOSITION:
S-GLASS EPOXY RESIN
TREATMENT:
IN CONTACT WITH
DIPROPYL ADIPATE
AT 76° F
RESULTS:
EXAMPLES OF TESTS
RUN AT VARIOUS
TIMES
BEAM:
1/2 T.

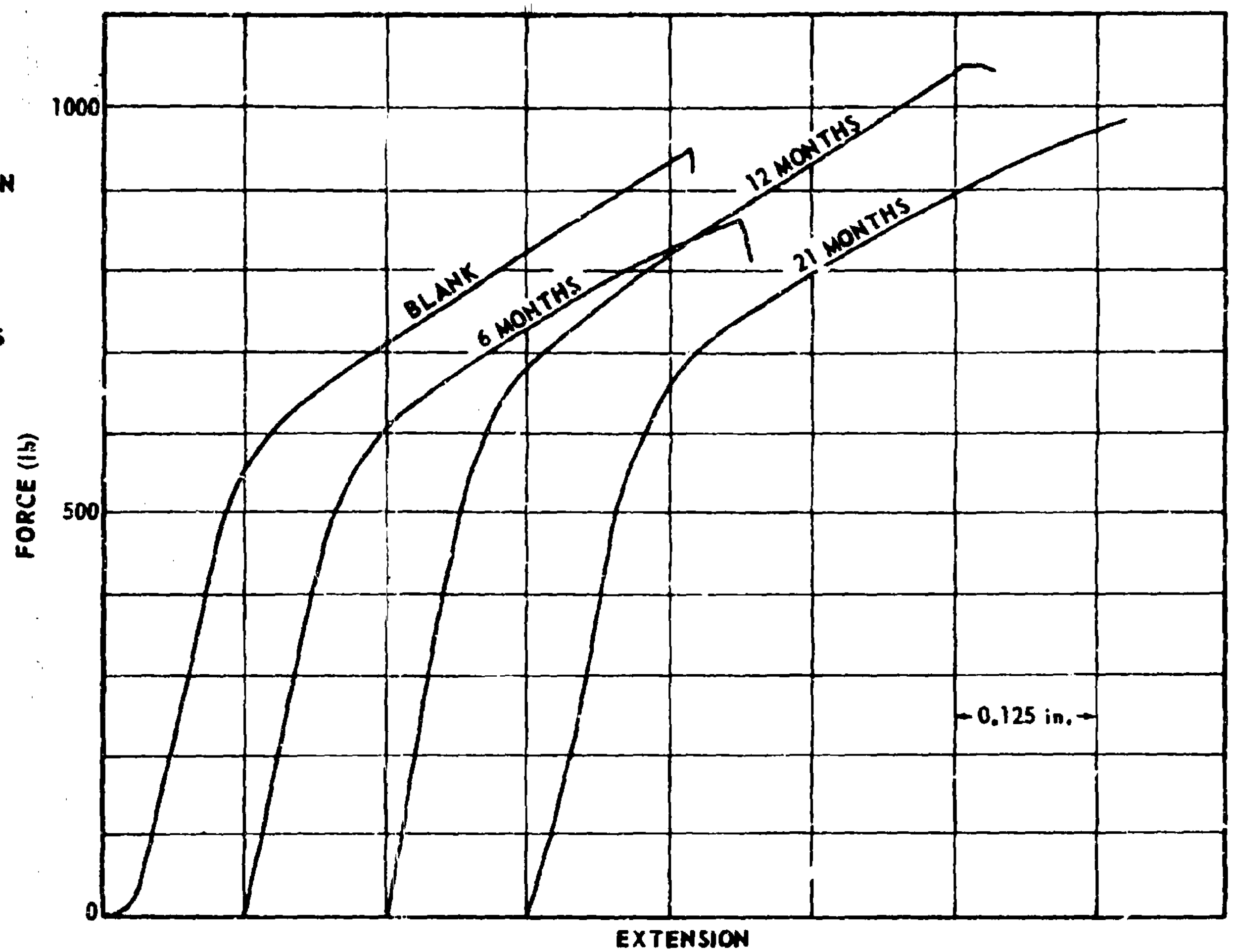

FIGURE 1. TYPICAL VARIATION IN THE STRESS-ELONGATION CURVES FOR RINGS IN CONTACT WITH DIPROPYL ADIPATE FOR VARIOUS LENGTHS OF TIME

MATERIAL:
COMPOSITE
COMPOSITION:
S-GLASS EPOXY RESIN
TREATMENT:
IN CONTACT WITH
PLASTICIZER AT 76° F
FOR 12 MONTHS
RESULTS:
EXAMPLES OF TESTS
ON VARIOUS
PLASTICIZERS
REMARKS:
1. BLANK
2. BUTYL PHTHALATE
3. PROPYL ADIPATE
BEAM:
1/2 T.

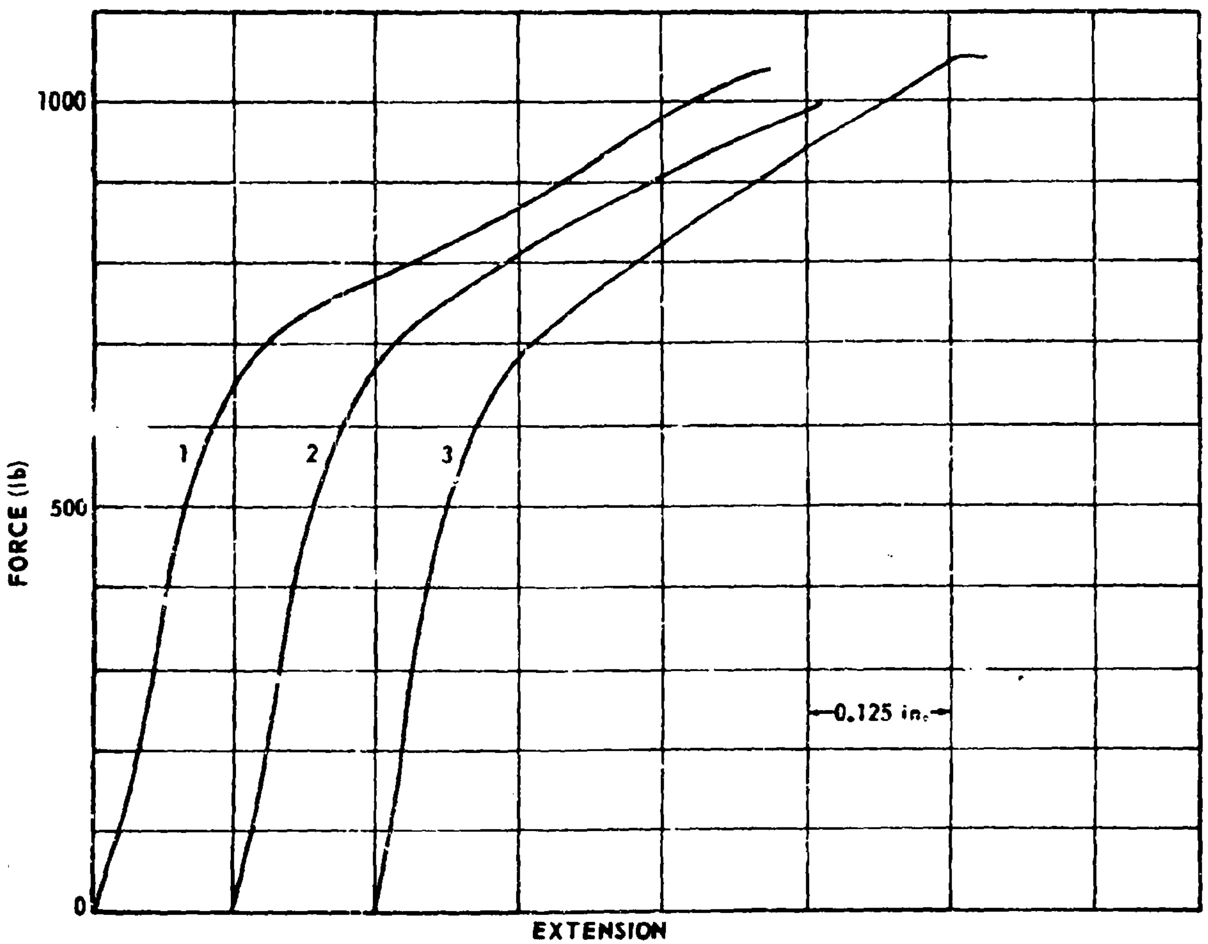

FIGURE 2. VARIATION IN THE STRESS-ELONGATION CURVES FOR VARIOUS PLASTICIZERS AT 12 MONTHS

TABLE II. EFFECT OF PLASTICIZERS ON BREAK STRENGTH AND ELONGATION AT BREAK AT 76°F

Plasticizer	Time (mo) 3		6		9		12		15		21	
	TS*	E**	TS	E	TS	E	TS	E	TS	E	TS	E
Blank	990	515	940	539	1010	500	830	564	(530)	(186)	810	485
	830	525	920	466	910	529	1040	559	1030	564	920	554
	(610)	(220)	940	495	940	529	1090	559	920	603	770	407
Tributyl phosphate	860	431	880	466	980	544	1010	505	900	431	950	456
	(670)	(392)	670	328	950	564	980	510	910	529	750	490
	870	544	630	270	790	529	650	397	1020	500	(710)	(358)
TEGDN	960	534	870	515	880	593	880	505	970	515	650	250
	770	549	990	500	990	520	1040	554	1000	544	840	456
	870	515	(570)	(206)	(480)	(147)	1200***	520	1000	544	840	539
Ethyl nonanoate	820	490	1010	505	760	426	1030	475	710	304	840	461
	940	495	1000	544	1030	466	760	534	1055	525	800	569
	880	441	890	490	1020	529	960	456	860	603	840	417
Dibutyl phthalate	1000	505	900	485	950	495	730	412	950	505	1010	451
	850	500	750	549	960	559	840	480	970	598	990	574
	690	387	730	456	850	446	660	309	910	554	940	554
Dipropyl adipate	790	368	910	446	(600)	(221)	1050	500	900	441	950	554
	890	402	790	436	720	412	880	564	950	520	1000	520
	870	520	870	436	880	461	610	348	910	495	730	402
Triethyl phosphate	(540)	(176)	(430)	(216)	930	485	(630)	(275)	990	480	940	490
	960	412	840	412	830	441	930	456	980	534	940	544
	920	539	750	412	980	515	920	451	710	456	1010	485

* Tensile strength is in pounds.

** Elongation is given in thousandths of an inch.

*** Estimated. Actual TS beyond the range of the instrument.

the breaking strength are in pounds. Values of the extension are in thousandths of an inch. The values in parentheses indicate that the ring broke in a resin poor area. The value therein is the actual value found. The value used in analysis was the average value of the two acceptable rings.

Table III gives similar data for samples stored at 140°F. The same units are used and the same usage for rings breaking in a resin poor area.

TABLE III. PLASTICIZERS VERSUS BREAK STRENGTH AND ELONGATION AT BREAK AT 140°F STORAGE

Plasticizer	Time (mo)					
	6		9		15	
	TS	E	TS	E	TS	E
Blank	870	529	980	505	890	407
	820	431	880	475	910	456
	990	495	-	(2 only)	1100	569
Dibutyl phthalate	960	461	1040	539	1100	490
	720	319	830	441	700	338
	990	490	740	402	830	495
Dipropyl adipate	940	941	1040	525	1040	485
	970	500	840	495	970	441
	920	466	850	475	930	500
Triethyl phosphate	(610)	(206)	870	466	930	539
	910	475	(520)	(147)	970	490
	800	505	1000	500	1000	520
Dibutyl maleate	1040	480	1010	515	1000	529
	990	569	1050	525	830	466
	650	333	970	495	620	377

Statistical analysis of the data on extension of Table II showed that both plasticizer and time are significant variables. A strong interaction was likewise found between plasticizer and time. Time was found to enter in a higher degree than linear. Results of this analysis for the different plasticizers are shown in Table IV. Values given are the summation of all extensions for a single plasticizer.

TABLE IV. RATING OF RINGS BY EXTENSIONS AT BREAK

Rings		
Blank	10.92*	90%
TEGDN	10.64	
DBP	10.27	
EN	10.24	
TEP	9.95	
TBP	9.86	
DPA	9.81	

* Values given under the Rings are the sum of extensions at break for all rings of that class. It is the summation of values for 21 rings.

The statistical interaction between time and plasticizer was examined further. It was noticed that a pronounced minimum, statistically significant, occurred for each plasticizer except ethyl nonanoate. These minima occurred at various time intervals. The minimum for dipropyl adipate occurred at 3 months, those for tributyl and triethyl phosphate occurred at 6 months, that for dibutyl phthalate occurred at 12 months, and those for the blank and for TEGDN at 21 months. The time of the minimum can be related to the effect of the plasticizer inasmuch as the later the time of the minimum, the greater the sum of the extensions at break, i.e., the less the effect of the plasticizer.

These minima are probably related to the rates of diffusion of the various plasticizers, either through the plastic or along the plastic-glass interface. The fact of the minimum can be explained if it is assumed that the front of the plasticizer penetration divided the ring into two layers, whose strengths are not additive but are approximately equal. The small differences in extension and the relatively large standard error prevent a meaningful correlation between physical properties of the plasticizers and the extension.

An analysis was made of the data on extension at 140°F (Table III). No significant differences were found between plasticizers or between times at 140°F. A significant difference was found between temperatures, using corresponding times and plasticizers in Tables II and III.

5. Conclusions

Extension at break is capable of separating plasticizers at least into two groups, those which have no effect and those which do.

The differences in conditions of the experiment in Phase I and Phase II are such that different factors have become important. Neither the grouping of the plasticizers nor their order within groupings is the same.

Phase III of the experiment is now under way. In this phase pressure bottles of the same lot as in Phase I or Phase II will be packed with plasticizer and inert material, and these samples of each plasticizer will be burst hydraulically at intervals of 6 months.

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13. ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Glass-fiber-reinforced motor case rings						
Triethylene glycol dinitrate						
Tributyl phosphate						
Trethyl phosphate						
Dipropyl adipate						
Dibutyl phthalate						
Dibutyl maleate						
Ethyl nonanoate						
Deterioration						